Preface

Paul trap mass spectrometers are 3 dimensional, 3 electrode devices (consisting of a central ring electrode and two end cap electrodes) used for mass analysis of unknown samples The electrodes are machined to have a hyperbolic geometry Ions of the analyte gas are trapped between these electrodes when an rf potential is applied between the ring electrode and the end cap electrodes Ion motion within the trap is described by the linear Mathieu equations and ion stability is determined by two Mathieu parameters, a_u and q_u, on a Mathieu stability plot The trapped ions oscillate in the radial and axial directions with characteristic frequencies, referred to as the ion's radial and axial *secular* frequencies, which are dependent on a parameter β_u which can be determined from a_u and q_u This thesis addresses two problems related to ion resonance in weakly nonlinear Paul traps The first is the problem related to experimental observations of nonlinear resonance that causes unexpected ejection of ions from the nominally stable region of the Mathieu stability plot Such resonances occur when the secular frequency of the ion or its overtones match the sideband frequencies, which in turn occurs due to the interaction of the applied rf drive frequency with the secular frequency The second problem taken up for investigation in this thesis concerns the behavior of ions during resonance ejection when ion secular frequency is brought into resonance with an external excitation applied across the end cap electrodes Here, we will investigate the specific problem of improvement in mass resolution in resonant excitation experiments

This thesis has been divided into five Chapters Chapter 1 gives a brief introduction to Paul traps First, an overview of the trap operation has been presented Then, the equation of ion motion both under ideal and non ideal conditions is derived We next describe the concept of nonlinear resonance and the conditions under which it can take place Subsequently, we describe the phenomenon of resonant excitation The Chapter concludes by outlining the scope of the thesis

Chapter 2 presents results of our investigation of one nonlinear resonance in detail In particular, it deals with the nonlinear resonance occurring at a β_z value of $\frac{2}{5}$ (along the $a_u = 0$ axis) under the influence of a decapole and hexapole superposition We investigate the nonlinear Mathieu equation analytically by means of phase plots and Poincaré sections in order to understand the ion dynamics in the presence of hexapole and decapole nonlinearities It is found that decapole superposition has an effect at first order at $\beta_z = \frac{2}{5}$ while hexapole superposition has an effect only at third order Also the hexapole superposition induces a nonlinear resonance within a very narrow region of q_z

In Chapter 3 we first develop the equation of motion of an ion subjected to resonant excitation within the Dehmelt approximation regime ($q_z \leq 0\ 4$) The equation of motion under this approximation has the form of a forced damped Duffing equation with positive octopole nonlinearity This equation is analyzed using the method of harmonic balance and a frequency response curve which exhibits the jump phenomenon has been obtained We then extend the analysis to the nonlinear Mathieu equation with negative octopole nonlinearity The equation of ion motion has the form of a nonlinear Mathieu equation with additional damping and force terms The Harmonic Balance Based Averaging (HBBA) technique has been used to obtain the slow flow equations The equations thus obtained are used to generate a frequency response curve which has the same shape as the one obtained for the Duffing equation We then plot the phase portraits at different secular frequencies in order to visualize the actual dynamics undergone by the ions We see a saddle node bifurcation taking place at the frequency where the jump occurs

Chapter 4 presents a discussion on the results presented in Chapters 2 and 3 In particular it discusses the relevance of these results to mass spectrometry Nonlinear resonances result in erroneous mass spectra on account of unexpected ion ejection Under resonant excitation it is seen that, depending on the sign of nonlinearity, scanning the rf amplitude in one direction gives better resolved mass spectra and a scan in the opposite direction gives poorly resolved mass spectra

Chapter 5 presents a summary of the results

All references have been listed alphabetically at the end of the thesis